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CPO-27-M as heterogeneous catalysts for aldehyde cyanosilylation and styrene oxidation

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ABSTRACT

A series of isostructural 3D metal–organic frameworks of 2,5-dihydroxyterephthalate with different metal ions, CPO-27-M (or MOF-74-M, M = Co, Mg, Mn, Ni and Zn), have been studied as catalysts for cyanosilylation of aldehydes with trimethylsilylcyanide and oxidation of styrene with *tert*-butylhydroperoxide, and two mixed-metal Co-Mn MOFs also studied for cyanosilylation. All these MOFs are active in promoting cyanosilylation, but for styrene oxidation, only the Co and Mn MOFs are active while the others behave as initiators rather than catalysts. For both reactions, CPO-27-Mn exhibits the highest activity, and the catalytic processes are heterogeneous. Radical mechanisms were proposed for the styrene oxidation over CPO-27-Mn, which yields styrene oxide, benzaldehyde and a minor amount of phenylacetaldehyde. The cyanosilylation over CPO-27-Mn shows size selectivity towards aldehyde substrates, and the catalyst can be recycled without losing its structural integrity and catalytic activity. It is also recyclable for styrene oxidation, though the structure changes after the catalytic reaction.

1. Introduction

Metal–organic frameworks (MOFs) are a newly emerging class of porous materials that bear some intriguing features such as hybrid compositions, exceptionally high surface area, adjustable pore size as well as modifiable functionality [1,2], so they have brilliant prospects for applications such as gas adsorption/separation [3,4], drug delivery [5], chemical sensing [6], and heterogeneous catalysis [7–10]. Heterogeneous catalysts are highly desirable for several advantages in comparison with homogeneous ones, including easier recovery and recycle, less wastes and cleaner products. Furthermore, porosity can lead to enhanced reactivity and selectivity [10]. MOFs show great promise as new porous heterogeneous catalysts that can be alternative or complementary to conventional ones [10,11]. The catalytic sites of MOFs, either inherent in the frameworks or generated by post-synthetic methods [10,12], can be metal centers with unsaturated (or labile) coordination or any active groups attached to the frameworks. MOFs may also serve as host matrices encapsulating traditional catalysts such as nano-size metals, metal oxides and molecular catalysts [13–15].

The isostructural CPO-27-M (or MOF-74-M) series, of general formula $M_2(dhtp)$ (M = Co, Fe, Mg, Mn, Ni and Zn; H_4dhtp = 2,5-dihydroxyterephthalic acid), are 3D MOFs featuring 1D $[M(\mu\text{-}COO)(\mu\text{-}OH)]_n$ chains and honeycomb-like hexagonal channels with a free diameter of ~12 Å [16–23]. In the solvated forms, the channels are lined with coordinated water or DMF molecules. Upon desolvation, the metal coordination changes from octahedral to square pyramidal without compromising the framework integrity, leaving coordinatively unsaturated metal sites open to channels. The frameworks show good chemical stability, making them good candidates for heterogeneous catalysts. These materials represent a rare series of stable isostructural MOFs with a wide range of metals, offering a good opportunity to test the catalytic properties of different metal sites in almost identical environments. Furthermore, the isomorphism of these MOFs facilitates the preparation of mixed-metal catalysts with variable composition and tunable catalytic properties. However, catalytic studies with CPO-27-M are still rare, and the reactions studied have been limited to CO_2 cycloaddition of epoxides (M = Co, Mg) [24–26], aerobic or H_2O_2 oxidation of cyclohexene (M = Co, Ni) [27,28], dehydrogenation of ammonia borane (M = Mg, Zn) [29,30] and phenol hydroxylation (M = Fe) [31]. For comparison with MIL-101-Sc, CPO-27-Ni has recently been studied for the intermolecular carbonyl ene reaction of ethylglyoxylate and the Friedel–Crafts Michael addition of indoles to methylvinyl ketone [32].

We are interested in the catalytic properties of the CPO-27-M series for two important organic reactions: carbonyl

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cyanosilylation and styrene oxidation. Cyanosilylation of carbonyl compounds provides a convenient route to cyanohydrins, which are versatile intermediates that can be readily converted into industrially important compounds [33,34]. Cyanosilylation of aldehydes does not require strong Lewis acidity, and it is one of most frequently used model reactions for the study of MOFs as Lewis acid catalysts [10,35–39]. Catalytic oxidation of alkenes is a fundamental reaction that finds important applications in chemical industry. The oxidation of various substrates has been accomplished using metal-containing homo- or heterogeneous catalysts, including an increasing number of MOFs [27,28,40–48].

In this paper, we present a systematic study on the catalytic properties of different CPO-27-M catalysts (M = Co, Mg, Mn, Ni and Zn) for aldehyde cyanosilylation with trimethylsilylcyanide and styrene oxidation with *tert*-butylhydroperoxide. After comparative investigations on these different MOFs, we are focused on the most active catalyst to study the heterogeneity, size selectivity, recyclability and the possible mechanisms. The studies on two mixed-metal catalysts, CPO-27-$Mn_{0.57}Co_{0.43}$ and CPO-27-$Mn_{0.10}Co_{0.90}$, are also included to confirm the influence of different metal ions.

2. Experimental

2.1. Materials and catalyst preparation

The starting materials for catalyst synthesis [2,5-dihydroxyterephthalic acid (H_4dhtp) and various metal salts] and those for catalytic reactions [trimethylsilylcyanide (TMSCN), benzaldehyde, styrene, *tert*-butylhydroperoxide (TBHP, 5–6 M in decane)] were all used without further purifications. All of these materials except for TBHP (Sigma) were purchased from Sinopharm.

CPO-27-M catalysts were synthesized by the solvothermal procedures described in the literature. For M = Co, Ni, Mg, Zn, a mixture of tetrahydrofuran (THF) and water was used as solvent, and the metal sources are metal acetates or nitrates [21,49]; CPO-27-Mn was synthesized from manganese chloride with a mixture of *N*,*N*'-dimethylformide (DMF), ethanol and water as solvent [22]. The method for CPO-27-Mn was also successfully applied to CPO-27-Co. Two mixed-metal MOFs (solid solutions) were prepared as follows.

CPO-27-$Mn_{0.57}Co_{0.43}$. This compound was prepared according to the literature method for CPO-27-Mn. H_4dhtp (0.34 mmol, 67 mg), $MnCl_2·4H_2O$ (0.56 mmol, 110 mg), and $CoCl_2·6H_2O$ (0.56 mmol, 132 mg) were dissolved in a mixture of DMF, ethanol and water (13/1/1, v/v; 15 mL) in a 23 mL Teflon lined stainless steel autoclave and heated at 135 °C for 24 h. After cooling to room temperature, the solid was filtered out, washed with methanol three times, and dried in air. Yield: 90%. The metal contents in the product were determined by EDS analysis

CPO-27-$Mn_{0.10}Co_{0.90}$. This compound was prepared according to the literature method for CPO-27-Co. H_4dhtp (0.34 mmol, 67 mg) in THF (1.5 mL) and a solution of $Co(OAc)_2·4H_2O$ (0.56 mmol, 138 mg) and $Mn(OAc)·4H_2O$ (0.56 mmol, 136 mg) in H_2O (2 mL) were combined in the Teflon lined steel autoclave. The autoclave was sealed and heated in a pre-heated oven at 110 °C for 3 days. After cooling to room temperature, the solid was filtered out, washed with methanol three times, and dried in air. Yield: 85%. The metal contents in the product were determined by EDS analysis.

2.2. Characterization

The FT-IR spectra were recorded in the range 400–4000 cm^{-1} using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Powder X-ray diffraction data were collected on a Rigaku Ultima IV diffractometer equipped with Cu-Kα at a scanning rate of 10° min^{-1} in the 2θ range 3–50°. The accelerating voltage and the applied current were 35 KV and 25 mA, respectively. SEM study and the energy dispersive X-ray spectroscopy (EDS) analyses were carried out with a S-4800 HITACHI scanning electron microscope. Gas chromatography (GC) was conducted using a LingHua GC 9890E instrument equipped with an FID detector and an SE-54 capillary column (30 m × 0.25 mm × 0.25 μm).

2.3. Catalytic reaction

Generally, before a catalytic test, the as-synthesized MOFs were activated by the following solvent-exchange and heating procedures, if not specified otherwise. The MOFs were immersed and stirred continuously in methanol for 12 h, and then the liquid was decanted off. This methanol exchange procedure was repeated twice. The solid thus obtained was filtered, dried in air, transferred into a flask, heated at 170 °C for 4 h under dynamic vacuum, and cooled under nitrogen atmosphere to an appropriate temperature for the catalytic reaction. *n*-Dodecane was used as the internal standard for GC analysis. The temperature program for GC analysis was set as follows: the temperature was held at 40 °C for 1 min, then raised to 260 °C at 30 °C/min and held for 5 min. Inlet and detector temperatures were 280 °C.

2.3.1. Cyanosilylation of benzaldehyde

The catalytic reactions were carried out in dichloromethane (DCM) solutions under nitrogen atmosphere. The solvent was dried and distilled before use. In a typical catalytic experiment, DCM (15 mL), TMSCN (10 mmol), *n*-dodecane (5 mmol, as internal standard) and benzaldehyde (5 mmol) were added into the flask containing activated CPO-27-M (0.5 mmol). The mixture was stirred and refluxed in an oil bath. The reaction conversion was monitored by GC at different time intervals.

2.3.2. Styrene oxidation

In a typical reaction, the flask containing the activated catalyst was charged with a given amount of styrene (5 mmol), TBHP (5–6 M in decane, 15 mmol) and solvent (5 mL, if needed). The reaction mixture was stirred and kept at the given temperature under nitrogen atmosphere. Aliquot samples were withdrawn at different time intervals and immediately detected by GC.

3. Results and discussion

3.1. Characterization of the catalysts

The XRD patterns (Fig. 1a) of all as-synthesized products with different metal ions (Co, Ni, Mg, Zn, and Mn) are similar to one another and in good agreement with those reported elsewhere [21,22,49], indicating that the products are isostructural and have the desired CPO-27-type structures. The XRD profiles (Fig. 1b) of the samples activated by methanol exchange and subsequent vacuum heating at 170 °C showed no appreciable changes compared with those for the as-synthesized MOFs, confirming that the structural integrity of the frameworks is retained after activation.

Initially, CPO-27-Mn was synthesized by a solvothermal reaction for 24 h, according to a literature method [22]. However, we found that the compound can be obtained within a much shorter time, under otherwise identical conditions. The XRD pattern and the SEM picture of the sample obtained by reacting for 4 h are provided as Fig. S1 in Supplementary material. It is obvious that the crystalline phase can be well formed within the reduced time. Catalytic tests (*vide infra*) indicated that the catalysts synthesized within 4 and 24 h showed similar activity.

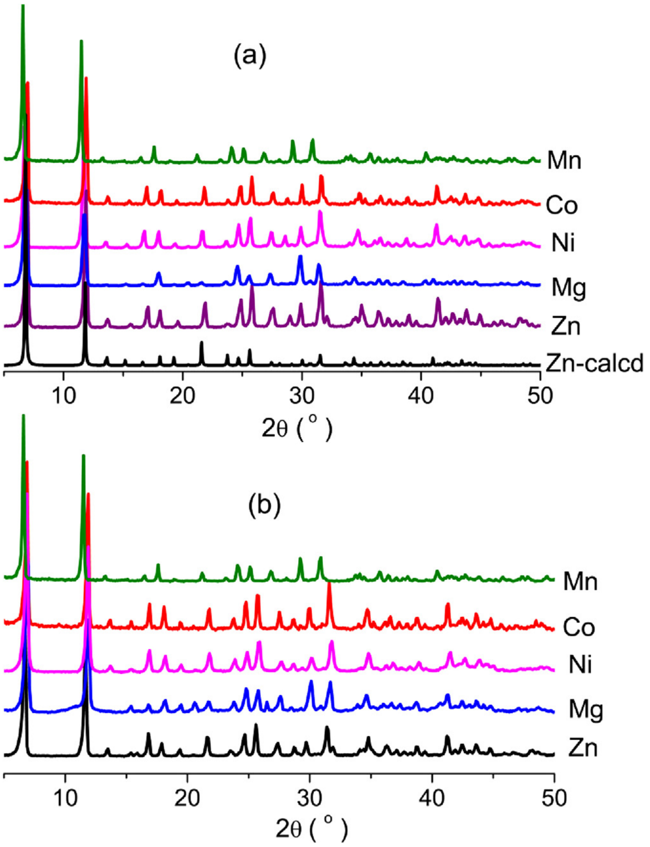


Fig. 1. XRD patterns of the as-synthesized (a) and activated (b) CPO-27-M MOFs.

We have also synthesized two mixed-metal MOFs, CPO-27-$Mn_{0.57}Co_{0.43}$ and CPO-27-$Mn_{0.10}Co_{0.90}$. XRD analysis indicated that they are isostructural with the parent MOFs (Fig. 2). Comparing the XRD patterns of the Co, Mn and Mn_xCo_{1-x} MOFs, one can see that the reflection peaks show systematic shifts towards low angles as the Mn content increases, consistent with the fact the ionic radius of Mn(II) is larger than that of Co(II). No splitting or broadening was observed for the peaks of mixed-metal systems compared with the single-metal compounds. The results suggest that the mixed-metal materials are essentially single phases (solid solutions with randomly distributed metal sites), rather than mechanical mixtures of phase-separated Co and Mn MOFs.

3.2. Catalytic properties for cyanosilylation

The addition reactions of TMSCN to benzaldehyde (Scheme 1) were carried out to compare the catalytic performance of the different CPO-27-M MOFs (M = Co, Ni, Mg, Zn, Mn). The time dependence of benzaldehyde conversion is shown in Fig. 3a and selected data are given in Table 1.

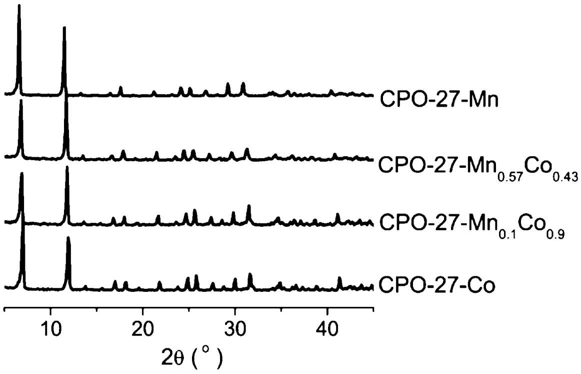
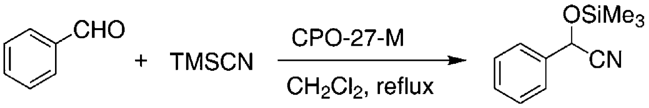


Fig. 2. XRD patterns for mixed-metal MOFs and the parent materials.



Scheme 1. Cyanosilylation of benzaldehyde.

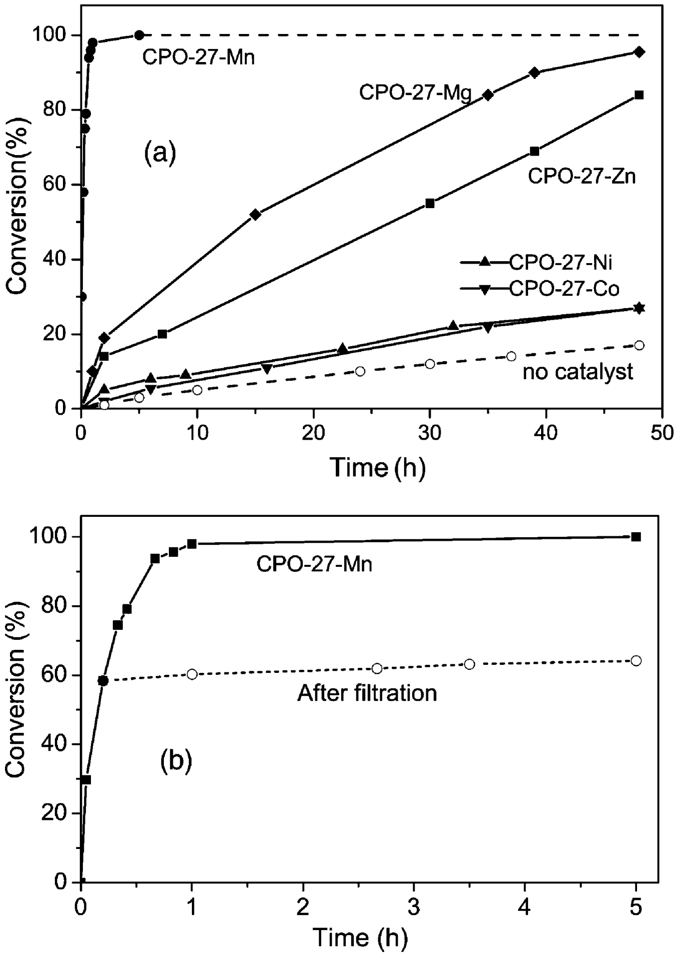


Fig. 3. Conversion vs. time plots for benzaldehyde cyanosilylation. (a) Reactions with and without CPO-27-M catalysts. (b) CPO-27-Mn-catalyzed reactions with and without filtering off the catalyst. *Conditions*: benzaldehyde, 5 mmol; TMSCN, 10 mmol; DCM, 15 mL, reflux; cat., 0.5 mmol (if used).

In all cases, the reactions of benzaldehyde with 2 molar equivalent of TMSCN in the presence of activated CPO-27-M yielded only the cyanosilylation product. Clearly, the catalytic activity is strongly dependent upon the nature of the metal ion in the catalyst. CPO-27-Co and -Ni show comparable activity with a conversion of ~27% within 48 h, which is higher by only 10% than the conversion for the blank test in the absence of any catalyst under otherwise identical conditions. CPO-27-Zn and -Mg are more active, giving much higher conversions within 48 h (83% and 96%, respectively).

Remarkably, CPO-27-Mn showed much higher activity than the above materials, the reaction reaching almost completion within 1 h. The CPO-27-Mn catalyst was prepared by a solvothermal method using DMF as solvent (with a small amount of ethanol and water), while the other catalysts used in the above comparison were obtained by the solvothermal synthesis in a mixture of THF and water. Therefore, it should be clarified whether the exceptional activity of the Mn MOF is related to its special synthetic

Table 1

Comparison of different catalysts for the cyanosilylation of benzaldehyde.[a]

Entry	Catalyst	Time (h)[f]	Conv. (%)[f]
1	Without catalyst	2, 48	~1, 17
2	CPO-27-Co[b]	2, 48	~2, 27
3	CPO-27-Ni	2, 48	5, 27
4	CPO-27-Zn	2, 48	14, 83
5	CPO-27-Mg	2, 48	19, 96
6	CPO-27-Mn	1	100
7	CPO-27-Co[c]	2, 48	3, 25
8	CPO-27-$Mn_{0.57}Co_{0.43}$	1	65
9	CPO-27-$Mn_{0.10}Co_{0.90}$	1, 2	5, 9
10	CPO-27-Mn + py[d]	1	38
11	CPO-27-Mn+ pyO[e]	1	24
12	$MnCl_2$[g]	1	44
13	H_4dhtp	1, 48	~0, 17

[a] *Conditions*: benzaldehyde, 5 mmol; TMSCN, 10 mmol; DCM, 15 mL, reflux; cat., 0.5 mmol (10 mol%).

[b] The CPO-27-Co catalyst was prepared by a solvothermal procedure with THF-water as solvent.

[c] The CPO-27-Co catalyst was prepared by a solvothermal procedure with DMF-ethanol-water as solvent.

[d] In the presence of pyridine (5 mmol).

[e] In the presence of pyridine *N*-oxide (3.5 mmol).

[f] For some entries, more than one conversion data obtained for different time periods (separated by commas) are provided for convenience of comparison.

[g] The amount of $MnCl_2$ was 1.0 mmol so that the metal content is the same as that of the MOF catalysts.

Table 2

The influence of synthetic time and post-synthetic treatment on the catalytic activity of CPO-27-Mn.[a]

Entry	Synthetic time (h)[b]	Methanol exchange	Heating	Time (h)[c]	Conv. (%)[c]
1	24	–	–	10	90
2	24	+	–	10	>99
3	24	–	+	3	>99
4	24	+	+	0.2, 1	58, >99
5	4	+	+	0.2, 1	60, >99

[a] *Conditions*: benzaldehyde, 5 mmol; TMSCN, 10 mmol; DCM, 15 mL, reflux; cat., 0.5 mmol (10 mol%). "+", the treatment was applied; "–", the treatment was not applied.

[b] The time duration of solvothermal reactions for the synthesis of the catalyst.

[c] For some entries, more than one conversion data obtained for different time periods (separated by commas) are provided for convenience of comparison.

method. For this purpose, it is desirable to compare the CPO-27-Mn catalysts prepared by different methods. However, our efforts to synthesize CPO-27-Mn using the THF-water method proved to be unsuccessful. Nevertheless, the DMF method for CPO-27-Mn has been successfully used to prepare CPO-27-Co, making it possible to compare the CPO-27-Co catalysts obtained by two different methods. It proved that the two samples led to similar conversions (Table 1, entries 2 and 7), so it may be said that the different synthetic methods do not significantly influence the catalytic performance.

To confirm that the remarkable difference in catalytic activity of the CPO-27-M MOFs is associated with the different metal centers, two mixed-metal MOFs, CPO-27-$Mn_{0.57}Co_{0.43}$ and CPO-27-$Mn_{0.10}Co_{0.90}$, which had been confirmed to be isostructural with the parent Co and Mn MOFs (Fig. 2), were tested for the same catalytic reaction. As can be seen from Table 1 (entries 8 and 9), the catalytic activity of the mixed-metal catalysts lies between the Co and Mn catalysts and increases with the Mn content. This confirms that it is the Mn(II) ion that is responsible for the remarkably high activity of CPO-27-Mn.

The most active CPO-27-Mn was compared with a simple salt, manganese chloride. Under the same conditions, the salt is also active for cyanosilylation but led to a much lower conversion than CPO-Mn-27 (Table 1, entry 12. A comparison of the conversion vs. time plots is given as Fig. S2 in Supplementary material). It is obvious that the Mn MOF is superior to the salt in catalyzing the cyanosilylation reaction. The organic precursor, H_4dhtp, was also tested. It turned out that the weak acid does not promote the reaction (Table 1, entry 13): no conversion was detected after 1 h, and the conversion after 48 h was the same as that for blank test.

The catalysts used in the above catalytic experiments were activated by a general post-synthetic procedure (methanol exchange followed by heating treatment, see the experimental section). The CPO-27-Mn samples obtained by different post-synthetic procedures were also tested (Table 2, entries 1–4). As can be seen, even the as-synthesized catalyst (no methanol exchange and no heating treatment before the catalytic test) shows significant activity for the cyanosilylation reaction, the conversion reaching 90% after 10 h (entry 1). This observation may indicate that the solvent molecules coordinated to the metal centers are labile to some degree. The methanol treatment before use leads to enhanced activity, with almost complete conversion after 10 h (entry 2). The heating treatment is more efficient in enhancing the activity: the reaction time required to achieve completion was dramatically reduced to 3 h (entry 3). The reaction time is further reduced to 1 h when both methanol exchange and subsequent heating treatment are applied to the catalyst (entry 4). These results indicate that the successive post-synthetic treatments can efficiently activate the catalyst and that the heating procedure is especially important in generating open metal sites. Hereafter in this paper, the fresh catalysts were all subjected to the general activation treatments. Table 2 also gives the catalytic data for the CPO-27-Mn sample synthesized by performing the solvothermal reaction for only 4 h (entry 5). It seems that the catalytic activity is not sensitive to the synthetic time, at least in the range of 4–24 h. Therefore, the CPO-27-Mn catalyst can be synthesized by a relatively time-saving procedure and activated by mild and simple treatments.

To demonstrate whether the catalytic activity of the Mn MOF is due to active sites in the solid phase or to any active species leaching into the liquid phase, a control filtration test was carried out. After a reaction over CPO-27-Mn proceeded for 12 min (58% conversion), the catalyst was removed by hot filtration, and the filtrate was refluxed again and monitored by GC analysis at different time intervals. The plot of benzaldehyde conversion vs. time is given in Fig. 3b, compared with the data for the reaction without filtration. The very small increase of the conversion after filtration could be attributed to a thermally activated slow reaction. The results suggest that there is no appreciable leaching of active species into the liquid phase and that the catalytic mechanism of the Mn MOF is heterogeneous in nature.

To provide further evidence for the existence of Lewis acidic sites (open metal centers) in CPO-27-Mn, control experiments were performed in the presence of CPO-27-Mn and catalyst poisons (Table 1, entries 10 and 11). The conversions of benzaldehyde after 1 h were dramatically decreased from 100% (in the absence of poisons) to 38% and 24% in the presence of pyridine and pyridine oxide, respectively. These results can be easily explained by the poisoning of the Lewis acid sites by strong interactions with pyridine or pyridine oxide.

With the above experimental results, on can safely say that the cyanosilylation reaction over CPO-27-Mn is a Lewis-acid catalyzed process. The mechanism could be similar to that proposed elsewhere [34,39]. The open Mn(II) center interacts with the oxygen atom of benzaldehyde, thus the carbonyl group is further polarized to facilitate the nucleophilic addition by the cyanation agent. The size effects of aldehyde substrates (see below) indicates that the reaction mainly occurs within the channel of the catalyst.

The recyclability of the CPO-27-Mn catalyst was also tested (Fig. 4). After the first reaction run (complete conversion, 1 h), fresh benzaldehyde (5 mmol) and TMSCN (5 mmol) were added into the

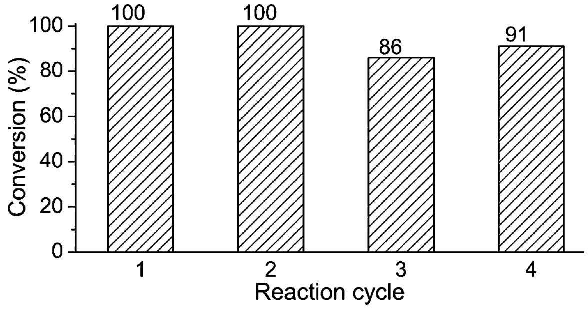


Fig. 4. Recycling tests of CPO-27-Mn for benzaldehyde cyanosilylation. *Conditions*: benzaldehyde, 5 mmol; TMSCN, 10 mmol; DCM, 15 mL, reflux; cat., 0.5 mmol; 1 h.

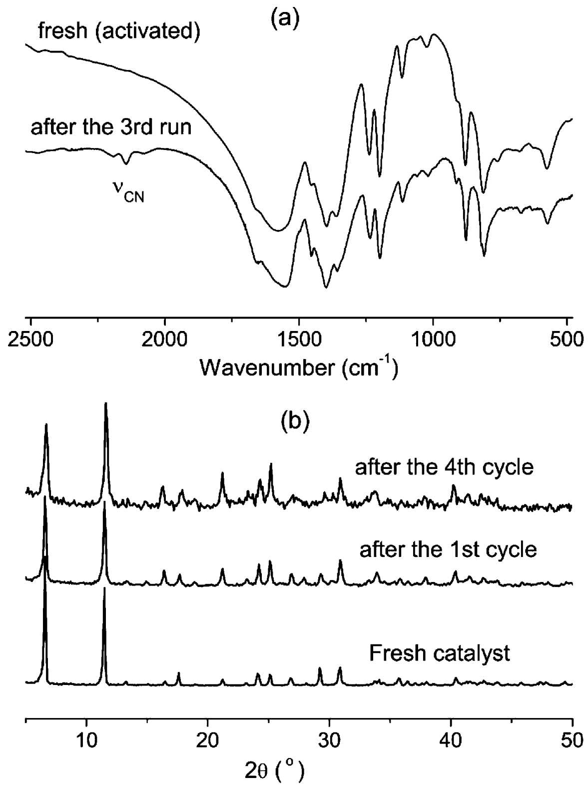
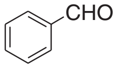
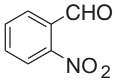
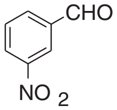
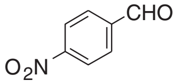
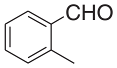
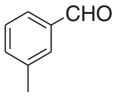
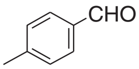
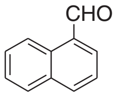
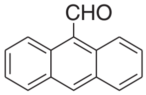
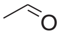
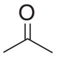
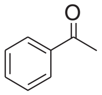


Fig. 5. IR spectra (a) and XRD profiles (b) of the CPO-27-Mn catalyst before and after the cyanosilylation reaction.

Table 3

CPO-27-Mn catalyzed cyanosilylation of various aldehydes and ketones.[a]

Entry	Carbonyl substrate	Time (min)	Conv. (%)
1		60	~100
2		30	~100
3		35	~100
4		5	~100
5		60	89
6		60	97
7		60	66
8		60	61
9		60	21
10		5	~100
11		60	11
12		60	17

[a] *Conditions*: substrate, 5 mmol; TMSCN, 10 mmol; DCM, 15 mL, reflux; cat., 0.5 mmol (10 mol%).

refluxing reaction mixture without separating out the catalyst and the product. It proved that the catalyst remained highly active with 100% conversion of benzaldehyde after 1 h. If the procedure was repeated for the third run, the conversion after 1 h was 86%. The reduced conversion in the third run could be due to the accumulation of product in the voids of the MOF. To support this assumption, the IR spectrum of the catalyst isolated after the third run was recorded and compared with that of the fresh catalyst (Fig. 5a). The used catalyst shows two new bands at 2192 and 2145 cm^{-1}, attributable to the $\nu(C{\equiv}N)$ absorption of the TMSCN reactant and the cyanosilylation product, respectively. The used catalyst after the third run was washed several times with DCM (until no signals except that of DCM were detected by GC) and then reused for the fourth run. The conversion in 1 h was increased to 91%. The somewhat lower conversion compared with the fresh catalyst could be due to the solid loss during the treatment. The recycling experiments indicate that the CPO-27-Mn catalyst can be reused with no need of heating reactivation and with no significant loss of activity. The XRD profiles of the catalysts isolated after the first and fourth runs are compared with that of the fresh catalyst in Fig. 5b. The crystalline phase of the catalyst is essentially retained after four cycles of reactions.

Furthermore, the CPO-27-Mn catalyst was applied to the cyanosilylation of other carbonyl substrates (Table 3). It proved that CPO-27-Mn is highly active towards mono-substituted benzaldehydes. The three nitrobenzaldehydes show much higher reactivity than benzaldehyde, reflecting the strong electron-withdrawing effects of the nitro group. The weak electron-donating effects of the methyl group were evidenced by the fact that the three methylbenzaldehydes show somewhat lower reactivity than benzaldehyde. It is noted that the electronic effects are more significant for *para*-substituted substrates, with *p*-nitro- and *p*-methylbenzaldehydes showing the highest and lowest reactivity, respectively, among the mono-substituted benzaldehydes studied. *p*-Nitrobenzaldehyde can reach complete conversion within as short as 5 min. The effects of substituent positions are open to further investigations.

The catalyst shows size selectivity towards the substrates. In comparison with the complete conversion of benzaldehyde, the

Table 4
Influence of catalyst dose and temperature on benzaldehyde cyanosilylation over Mn-MOF and the comparison with selected MOFs studied elsewhere.[a]

Entry	Catalyst[b]	Catalyst dose (mol%)[c]	Temp. (°C)	Time (h)[d]	Conv. (%)[d]	Ref.
1	CPO-27-Mn	2	40	1	63	This work
2	CPO-27-Mn	5	40	1	90	This work
3	CPO-27-Mn	10	40	1	~100	This work
4	CPO-27-Mn	4.5	r.t.	2, 5	30, 78	This work
5	CPO-27-Mn	10	r.t.	1, 4	54, 94	This work
6	$[Cd(bpy)_2](NO_3)_2$	20	40	24	77	[36]
7	$[Sm(H_2L)(H_3L)]$	10	r.t.	16	69	[40]
8	$Cu_3(BTC)_2$	15.8	40	48	50	[41]
9	$Mn_3[(Mn_4Cl)_3(BTT)_8]_2$	11	r.t.	9	98	[42]
10	$Sc_2(C_4O_4)_3$	4	r.t.	5, 12	45, 90	[43]
11	[Nd(BTC)]	4.5	r.t.	2	99	[44]
12	[Ho(BTC]	4.5	r.t.	2	76	[44]
13	[Er(BTC)]	4.5	r.t.	5	61	[44]
14	[Yb(BTC)]	4.5	r.t.	5	57	[44]
15	$[Zn_3(bpy)_{3.5}(O_2CH)_4](ClO_4)_2$	13	25	24	22	[45]
16	$[Cd(L')_2(ClO_4)_2]$	5	r.t.	14	92	[38]

[a] All the catalytic reactions were performed with a 1:2 molar ratio of benzaldehyde to TMSCN in DCM.

[b] H_4L = 2,2′-diethoxy-1,1′-binaphthalene-6,6′-bisphosphonic acid, BTC = benzene 1,3,5-tricarboxylate, H_3BTT = 1,3,5-benzenetristetrazol-5-yl, L′ = bis(4-imidazol-1-yl-phenyl)diazene, bpy = 4,4′-bipyridine.

[c] The catalyst doses all correspond to the molar amount of the metal ion relative to benzaldehyde.

[d] For some entries, more than one conversion data obtained for different time periods (separated by commas) are provided for convenience of comparison.

conversion of 1-naphthaldehyde dropped dramatically to 61% under the same conditions, and for the still larger substrate 9-anthrylaldehyde, the conversion was further decreased to only 21%. The size effect could suggest that the cyanosilylation reaction occurs mainly within the open channels of the MOF catalyst.

For acetaldehyde, the catalyst shows high activity similar to that for *p*-nitrobenzaldehyde, the conversion reaching completion within as short as 5 min. For acetone and acetophenone, the activity is much lower due to the low reactivity of ketones compared with aldehydes.

A number of MOFs have been studied as catalysts for cyanosilylation of benzaldehyde and its derivatives. It is desirable to compare the performance of CPO-27-Mn with that of other MOFs studied previously. However, the reaction conditions used (catalytic dose, temperature, solvent, reaction time, the reactant ratio and even the substrate) are diverse so that it is impossible to make a meaningful comparison covering all the MOFs studied. To make the comparison to cover more (but not exhaustive) MOFs, we have performed additional reactions of benzaldehyde with TMSCN by varying the catalytic dose and the reaction temperature. As expected, the conversion within 1 h increases with the amount of the catalyst and with the temperature (Table 4, entries 1–5). The data reported for other MOF catalysts studied under comparable conditions [35,37,50–55] are also collected in Table 4. As can be seen, CPO-27-Mn is among the most active MOF catalysts for cyanosilylation addition. It is more active than most of the catalysts listed, including the Cd(II)/Zn(II) coordination polymers with neutral N-donor ligands (entries 6, 15 and 16), some MOFs with 1,3,5-benzenetricarboxylate (BTC) (entries 8, 13 and 14), the Sm(III) compound with a phosphonate ligand (entry 7), a Sc(III) species with squarate (entry 10) and the Mn(II) MOF with a tritetrazolate ligand (entry 9). Only the Nd(III) and Ho(III) MOFs with BTC (entries 11 and 12) show higher activity than CPO-27-Mn.

3.3. Catalytic properties for styrene oxidation

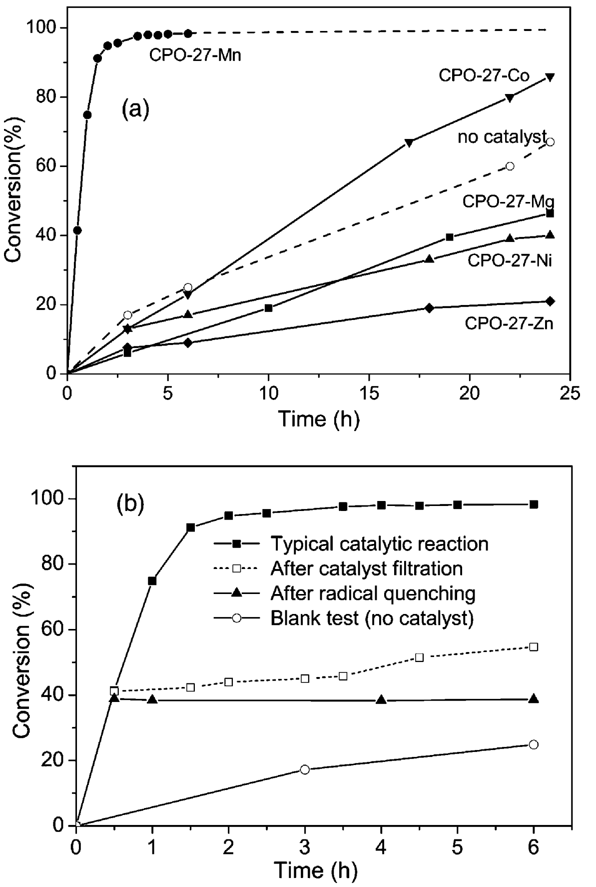


Fig. 6. Conversion vs. time plots for styrene oxidation. (a) Reactions with and without CPO-27-M catalysts. (b) CPO-27-Mn-catalyzed reaction and the control tests with catalyst filtration, with radical quenching, and without catalyst. *Conditions*: cat., 0.25 mmol (if used); styrene, 5 mmol; TBHP (5–6 M in decane), 15 mmol; 75 °C.

First, we compared the catalytic ability of five CPO-27-M MOFs with different metal ions under "solvent-free" conditions (except for the decane introduced together with TBHP, no solvent was added into the reaction mixture). The time dependence of styrene conversion is shown in Fig. 6a and selected data of conversion and selectivity are collected in Table 5. As can be seen, the Mn and Co MOFs show different activities for the oxidation reaction, but the Mg, Zn and Ni MOFs are inactive and even have inhibition effects because the conversions in the presence of these MOFs are lower than that for the thermally activated reaction in the blank test (no catalyst). The Co MOF also plays an inhibiting role in the initial stage but becomes active after a long induction time. Although the mechanism of the inhibition effects is unclear, the activity of the Mn and

Table 5
Catalytic data for the oxidation of styrene over different CPO-27-M MOFs.[a]

Entry	Catalyst	Time (h)	Conv (%)	Selectivity (%)		
				A	B	C
1	CPO-27-Mn	2	95	38	55	7
2	CPO-27-Co	24	86	68	26	6
3	CPO-27-Ni	24	41	61	26	13
4	CPO-27-Mg	24	46	65	23	12
5	CPO-27-Zn	24	21	55	29	16
6	No catalyst	24	67	63	31	6
7	$MnCl_2$[b]	2	74	49	47	4

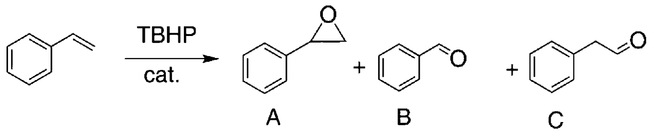
[a] *Conditions*: catalyst, 0.25 mmol (5 mol%); styrene, 5 mmol; TBHP (5–6 M in decane), 15 mmol; 75 °C. A = styrene oxide, B = benzaldehyde, C = phenylacetaldehyde.

[b] The amount of $MnCl_2$ was 0.5 mmol so that the metal content is the same as that of the MOF catalysts.

Table 6
Effect of solvents on the oxidation of styrene.[a]

Entry	Solvent	Conv. (%)	Selectivity (%)		
			A	B	C
1	"Solvent free"	95	38	55	7
2	Acetonitrile	69	27	70	3
3	DCE	58	33	60	7
4	*n*-Decane	51	29	64	7
5	Benzene	44	30	59	11
6	*n*-hexane	31	31	64	5
7	DMF	12	36	63	1
8	Ethanol	11	32	67	1

[a] *Conditions*: catalyst, 0.25 mmol; styrene, 5 mmol; TBHP (5–6 M in decane), 15 mmol; solvent, 5 mL; 75 °C, 2 h; DCE = 1,2-dichloroethane, DMF = *N,N'*-dimethylformide; A = styrene oxide, B = benzaldehyde, C = phenylacetaldehyde.



Scheme 2. Oxidation of styrene catalyzed by CPO-27-M.

Co species and the inactivity of the Zn, Mg and Ni analogs are in agreement with the different ability of these divalent metal ions in changing their oxidation state. A previous study has also revealed that the same Co MOF can catalyze the aerobic oxidation of cyclohexene while the Ni analog is totally inactive [27]. Notably, our results suggest that the Mn MOF is much more active (95% conversion after 2 h) than the Co analog (86% conversion after 24 h). This trend is qualitatively consistent with the fact that Mn(II) is easier to be oxidized than Co(II).

The most active Mn MOF has been compared with $MnCl_2$ for the oxidation reaction (Table 5, entry 7. A comparison of the conversion vs. time plots is given in Fig. S3 in Supplementary material). Ii turned out that he chloride salt is less active than CPO-27-Mn. During the reaction using the salt, partial dissolution of the solid was observed, and a filtration control test suggests that the catalysis with the salt is homogeneous (see Fig. S3 in the supplementary material).

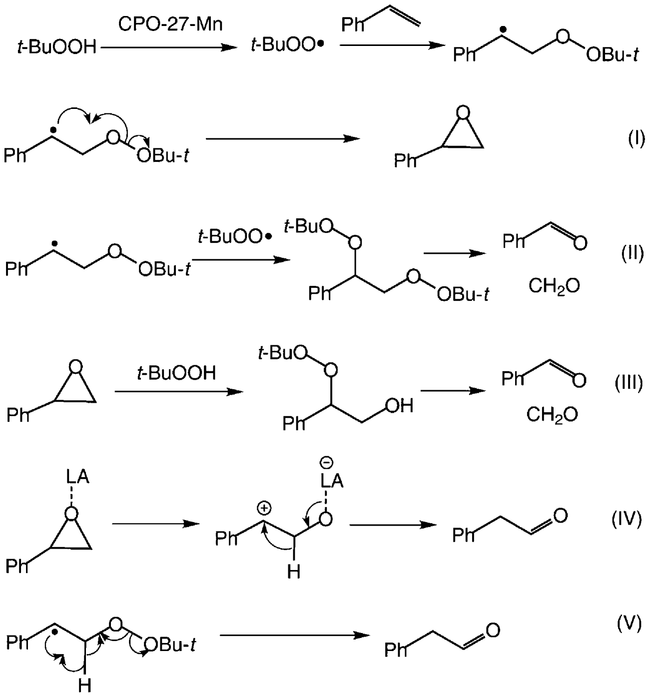
As shown in Table 5, the oxidation of styrene under the given conditions yielded styrene oxide (A), benzaldehyde (B), and phenylacetaldehyde (C) (Scheme 2). The time dependence of the conversion and yields is shown in Fig. S4 (see Supplementary material) for CPO-27-Co and -Mn. In both cases, phenylacetaldehyde is a minor product (less than 10%). With CPO-27-Mn, the selectivity for benzaldehyde is always higher than that for styrene oxide, while CPO-27-Co favors styrene oxide. The effects of temperature, catalyst dose and oxidant dose on the styrene oxidation over CPO-27-Mn were tested (see Fig. S5 in Supplementary material). As expected, the conversion increases with these reaction parameters. As far as selectivity is concerned, benzaldehyde is favored at lower temperature. Using a large amount of the catalyst (3 mol% or more) or the oxidant (3 equivalents) also increases the selectivity of benzaldehyde.

The CPO-27-Mn catalyzed oxidation reactions were performed in various solvents for comparison with the "solvent-free" reaction. The results are compiled in Table 6. In all solvents used, the selectivity for different products decreases in the order of benzaldehyde > styrene oxide ≫ phenylacetaldehyde, as observed in the solvent-free case. The results obtained for decane (Table 6, entry 4) suggest that dilution has a strong negative effect on the catalytic activity. The conversions in highly polar solvents such as ethanol and DMF are much lower than those in the other solvents, perhaps because ethanol and DMF have a strong coordination ability and lead to the blocking of metal sites. For the rest of the solvents, it seems that a more polar solvent lead to a higher conversion (acetonitrile > 1,2-dichloroethane (DCE) > benzene > *n*-hexane). Nevertheless, the conversion of styrene in the presence of any of these solvents is significantly lower than that for the "solvent-free" reaction. Hereafter the oxidation was carried out under 'solvent-free' conditions.

The heterogeneous character of the styrene oxidation over CPO-27-Mn was checked. After a catalytic reaction was carried out for 0.5 h, the solid catalyst was filtered off from the hot mixture, and the filtrate was heated at the same temperature for some time. As shown in Fig. 6b, the reaction in the filtrate was much slower than the reaction without filtration. The slight increase of the conversion from 41% to 55% upon heating for 5.5 h after filtration is most likely due to non-catalytic thermal oxidation. As also shown in Fig. 6b, the blank reaction in the absence of any catalyst reaches a conversion of 23% after 6 h, confirming the occurrence of thermally activated oxidation. The above results suggest that the high reaction rate in the presence of CPO-27-Mn arises from the solid phase rather than leached species in the solution.

The possible mechanism for the oxidation reaction was also investigated. To probe if radicals were involved, a radical scavenger, butyl hydroxy toluene (BHT, 2,6-di-*tert*-butyl-4-methylphenol), was added after the CPO-27-Mn catalyzed reaction proceeded for 0.5 h. As can be seen from Fig. 6b, no further conversion of styrene was observed after the addition of BHT, indicating that both catalytic and non-catalytic processes were completely inhibited. The test suggests that the oxidation reaction proceeds via radicals. The radical mechanism for the catalytic formation of benzaldehyde and styrene oxide could be proposed as follows, similar to that for a Co(II) catalyst [48]. As shown in Scheme 3, TBHP reacts with the Mn(II) MOF to generate a *tert*-butylperoxy radical. Then the radical was added to the styrene double bond to generate a benzylic radical derivative, which undergoes oxygen migration to form the epoxide (and the *t*-BuOH byproduct) (route I) or reacts with the *tert*-butylperoxy radical to give benzaldehyde via oxidative C–C bond cleavage (route II).

Benzaldehyde may also be a secondary product coming from styrene oxide, the mechanism involving the ring-opening of styrene oxide with peroxides followed by C–C cleavage (route III) [56,57]. Concerning the formation of phenylacetaldehyde, it is often attributed to the Lewis-acid promoted ring-opening isomerization of styrene oxide [45,56,57], which involves a hydride migration (route IV) [58,59]. To gain information about the mechanism of aldehyde formation, we checked the product distribution of the above radical-inhibiting test and found no indications of the conversion of the epoxide product to aldehyde products (the amount of each product remained constant with time) after the styrene conversion was stopped by BHT. Furthermore, an independent control experiment was carried out, for which a mixture of



Scheme 3. Possible mechanism for the styrene oxidation over CPO-27-Mn.

styrene oxide, TBHP and CPO-27-Mn was allowed to react under the conditions used for styrene oxidation. No conversion of styrene oxide to aldehydes was detected. These results clearly suggest that both aldehydes are the primary products of styrene oxidation *via* radical-involving processes, rather than originating from the epoxide product, so routes III and IV could be ruled out. A possible mechanism for the formation of phenylacetaldehyde is that the benzylic radical immediate undergoes migration of a β-hydrogen to the benzylic carbon and simultaneous (or subsequent) O-O cleavage (route V).

Finally, the recyclability of CPO-27-Mn for the oxidation reaction was confirmed. The conversion of styrene remains at a high level for three successive reaction cycles (Fig. 7a) though XRD analysis indicated that the catalyst has lost the original structure and changed into an unknown phase after the first run (Fig. 7b). This represents a rare example of MOFs retaining the high catalytic activity after structural degradation. The catalytically active new phase derived from CPO-27-Mn is open to further investigations.

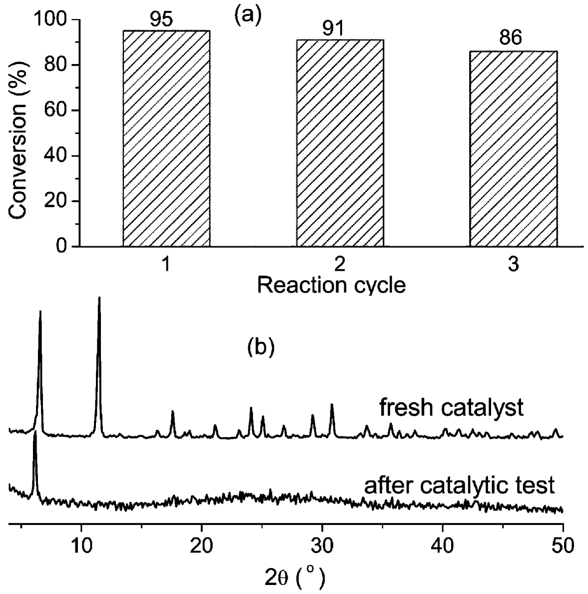


Fig. 7. (a) Conversion data of the recycling tests of CPO-27-Mn for the styrene oxidation (cat., 0.25 mmol; styrene, 5 mmol; TBHP (5–6 M in decane), 15 mmol; 75 °C, 2 h). (b) Comparison of the XRD profiles of CPO-27-Mn before and after the catalytic test.

4. Conclusions

In summary, we have presented a systematic study of using the isostructural CPO-27-M MOFs (M = Co, Mg, Mn, Ni, Zn, $Mn_{0.57}Co_{0.43}$, and $Mn_{0.1}Co_{0.9}$) as catalysts for two organic reactions, cyanosilylation of aldehydes with trimethylsilylcyanide and oxidation of styrene with *tert*-butylhydroperoxide. The catalytic performance is strongly dependent on the metal ion contained in the MOF. CPO-27-Mn is the most active for both reactions, while the Mg, Zn and Ni MOFs act as inhibitors rather than catalysts for the oxidation reaction. The CPO-27-Mn catalyzed cyanosilylation is heterogeneous and size selective towards aldehyde substrates, characteristic of a porous catalyst, and the catalyst retains the structural integrity and catalytic activity when recycled. Heterogeneity and reusability of CPO-27-Mn have also been confirmed for the oxidation reaction, though the structure changes after the reaction. After some intentional control tests, radical mechanisms were proposed for the formation of styrene oxide, benzaldehyde and phenylacetaldehyde from styrene. An extension of the study to more reactions is underway in this lab to further understand the great effects of different metal ions on catalytic performance of MOFs. Studies along this line may also open the possibility of using mixed-metal MOFs to tune catalytic properties and to develop catalysts for multicomponent or cascade reactions.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.06.040.

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